Organic Vapor Recovery and Energy Efficiency during Electric Regeneration of an Activated Carbon Fiber Cloth Adsorber

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Abstract: An electrothermal-swing adsorption system was demonstrated on the bench scale for capture and recovery of organic vapors from air streams. Methyl propyl ketone (MPK), methyl ethyl ketone, *n*-hexane, acetone, and methylene chloride were removed and recovered at 200–1,020 ppm_v in a 40.0 slpm air stream while using activated carbon fiber cloth (ACFC) adsorbent. Removal efficiencies were greater than 99.9%. Liquid recovery fractions increased with increasing relative pressure, ranging from 0.11 for methylene chloride ($P/P_{sat}=2.1\times10^{-3}$) to greater than 0.80 for MPK ($P/P_{sat}=2.2\times10^{-2}$). The electrical energy consumed during regeneration per mol of liquid organic compound recovered decreased with increasing relative pressure of the inlet gas stream, ranging from 4,698 kJ/mol for methylene chloride to 327 kJ/mol for MPK. Equilibrium ACFC adsorption capacity, throughput ratio, and length of unused bed were also evaluated. These results are encouraging for the development of a new technology to capture and readily recover a wide range of organic vapors from air streams.

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Introduction

The potential acute and chronic effects associated with the release of solvents and other volatile chemicals into the atmosphere have caused concern for their impact on human health and the environment. The U.S. EPA regulates the emission of solvents to the atmosphere, both for their direct impact on human health [where they are regulated as hazardous air pollutants (HAPs)] and for their implication in the formation of tropospheric ozone [where they are regulated as volatile organic compounds (VOCs)] (EPA 2000b). There is also growing concern about the release of other volatile chemicals because of their implication in greenhouse gas warming through the formation of tropospheric ozone (EPA 2002a).

The EPA estimates that 1.6×10^{10} kg of VOCs were emitted from anthropogenic sources in the United States during 2001, with industrial solvent utilization accounting for 28% of these emissions (EPA 2003). Industrial solvent source categories include degreasing, printing, dry cleaning, surface coating, and other applications (EPA 2000a). Many solvents cause or are suspected of causing cancer or other detrimental effects to human health and the environment, and are classified as HAPs (EPA 2000a). The Clean Air Act of 1990 defines maximum achievable control technology (MACT) standards for control of HAPs in various industrial sectors based on current control technologies, and it lists 188 HAPs that are governed by these standards (EPA 2000a,b). For existing stationary sources, the MACT standard is defined as the average emissions reduction achieved by the best 12% of sources in a category, if there are 30 or more existing sources in that category (EPA 2000b). For new sources, the MACT standard is defined by the best-controlled similar source in the sector (EPA 2000b).

Reduction in the amount of solvent emissions required to meet MACT standards can be accomplished with source reduction, material substitution, oxidative destruction, absorption, condensation, or adsorption. Capture and recovery of solvents offers a potentially cost-effective and environmentally beneficial means to control solvent emissions, as solvents can be recovered for process reuse, and energy costs can be lower than for existing technologies. Adsorbents that are typically used to capture and re-

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Table 1. Properties of Selected Organic Vapors

Compound	Formula	Normal boiling point at 101,000 Pa[a] (°C)	Saturation vapor pressure at 20°C[b] (P_{sat}, Pa)	Tested concentration range (ppm by volume)	Range of relative pressure tested (P/P_{sat})
MPK	$C_5H_{10}O$	102	3.47×10^3	250–1,000	7.4×10^{-3}–2.2×10^{-2}
MEK	C_4H_8O	79.6	9.33×10^3	200–750	2.2×10^{-3}–7.9×10^{-3}
n-hexane	C_6H_{14}	68.7	1.60×10^4	230–750	1.5×10^{-3}–4.5×10^{-3}
Acetone	C_6H_6O	56.5	2.45×10^4	500–1,020	2.1×10^{-3}–4.2×10^{-3}
Methylene chloride	CH_2Cl_2	40.7	4.65×10^4	960	2.1×10^{-3}

Note: MPK=methyl propyl ketone; MEK=methyl ethyl ketone.

[a]*Merck Index* (1996).

[b]Reid et al. (1987).

cover gas-phase emissions include activated alumina, silica gel, zeolites, and activated carbon. These adsorbents are typically regenerated with steam, inert gas, or a vacuum.

Activated carbon fiber cloth (ACFC) is a subset of activated carbon adsorbents that offers certain advantages over conventional granular activated carbons. The ACFC used here is ash-free, which does not promote undesirable chemical side reactions, and has a fiber diameter of 12.3 ± 1 μm, which provides rapid mass and heat transfer to minimize the risk of ignition within the adsorption vessel (Foster et al. 1992; Lordgooei et al. 1998; Lo 2002). Activated carbon fiber cloth is microporous with large pore volumes, allowing high adsorption capacities at low adsorbate concentrations (Cal et al. 1994; Lordgooei et al. 1998), and it is available in shapable woven fabrics allowing the construction of filter cartridges (Hayes and Joseph 1981; Sullivan et al. 2001). The electrical properties of ACFC allow for energy-efficient electrothermal desorption because electrical energy is deposited directly to the inside of the fibers via the Joule effect (Petkovska et al. 1991; LeCloirec et al. 1996; Lordgooei et al. 1998; Sullivan et al. 2001). Electrothermal heating of saturated ACFCs causes rapid desorption of the adsorbate resulting in an extremely concentrated effluent stream, which can condense into a recyclable product without the need for ancillary heat transfer devices (Sullivan et al. 2001).

This paper evaluates the performance of a bench-scale ACFC electrothermal-swing adsorption system for industrial solvents at relative pressures ranging over an order of magnitude. Relative pressure is defined as the vapor's partial pressure (P) divided by its saturation vapor pressure (P_{sat}). The partial pressure of a vapor existing in equilibrium with its liquid is called the saturation vapor pressure. The selected solvents, in order of increasing values of P_{sat}, were methyl propyl ketone (MPK), methyl ethyl ketone (MEK), *n*-hexane, acetone, and methylene chloride. These compounds have P_{sat} values ranging from 3.47×10^3 to 4.65×10^4 Pa at 20°C (Table 1). Hexane, MEK, and methylene chloride are classified by the EPA as HAPs (EPA 2002b). The adsorbates and electrothermal-swing adsorption system were evaluated over a single adsorption and electrothermal regeneration cycle and over a range of relative pressures to obtain data and parameters for scale-up and operation of an automated dual-vessel system.

Experimental Apparatus and Procedures

Breakthrough tests were performed to characterize the ability of ACFC to capture and recover organic vapors under a range of relative pressures with air as the carrier gas. An adsorbate-laden air stream was passed through an adsorber containing ACFC until complete breakthrough occurred. Equilibrium adsorption isotherms were derived from these breakthrough curves and compared to results that were provided by an independent gravimetric method. The efficiency of the ACFC adsorber was evaluated with parametrics such as the throughput ratio (*TPR*) and length of unused bed (*LUB*).

The ACFC was then regenerated by purging the vessel with N_2 and applying electric voltage across the ACFC. The electric circuit consisted of the four ACFC cartridges in series, with the current flowing through the ACFC in each cartridge (Fig. 1). The desorbed organic vapor collected as a liquid at the exit of the adsorption vessel. The effectiveness of the regeneration process was evaluated by means of the fraction of organic vapor recovered as a liquid and the electrical energy consumed during electrothermal regeneration of the ACFC.

The adsorbate-laden air stream was generated using a syringe pump (KD Scientific Model 200) and hypodermic needle to inject liquid organic compound (> 99.5% pure) into a stream of dry air (Fig. 2). Competitive adsorption between organic vapors and water vapor exists (Cal et al. 1995; Sullivan et al. 2001) but was not tested as part of this study. The flow rate of air was controlled with a mass flow controller (Tylan FC-262, RO-28). Evaporation of the organic compound into the air stream was made more uniform by injecting the liquid into a fixed piece of ACFC that was attached to the hypodermic needle. All adsorption tests reported here were completed with single-component organic vapors in air, without evaluating the system's ability to capture and recover multicomponent organic vapors in air. However, the system was shown to capture and recover a 500 ppm by volume toluene and 500 ppm by volume methyl isobutyl ketone mixture from air (Dombrowski 2001).

The adsorbate concentration was measured with a total hydrocarbon (THC) analyzer equipped with a flame ionization detector (FID, Baseline Industries Series 8800). For each adsorbate, the FID was calibrated with a certified span gas (Matheson, Inc.). A mass balance based on the flow rates of air and adsorbate was used to calculate the expected concentration produced by the gas generation system. The mass balance value served as a check on the FID output. Span gases were not available for MPK and acetone. In these cases, the FID was calibrated with MEK, and then a correction factor based on chemical structure was used to correlate the FID output to the actual MPK or acetone concentration as calculated by mass balance. In all tests except one, the concentrations were within 7% of their target value based on mass balances. In one test, the concentration was within 17.6% of the target value.

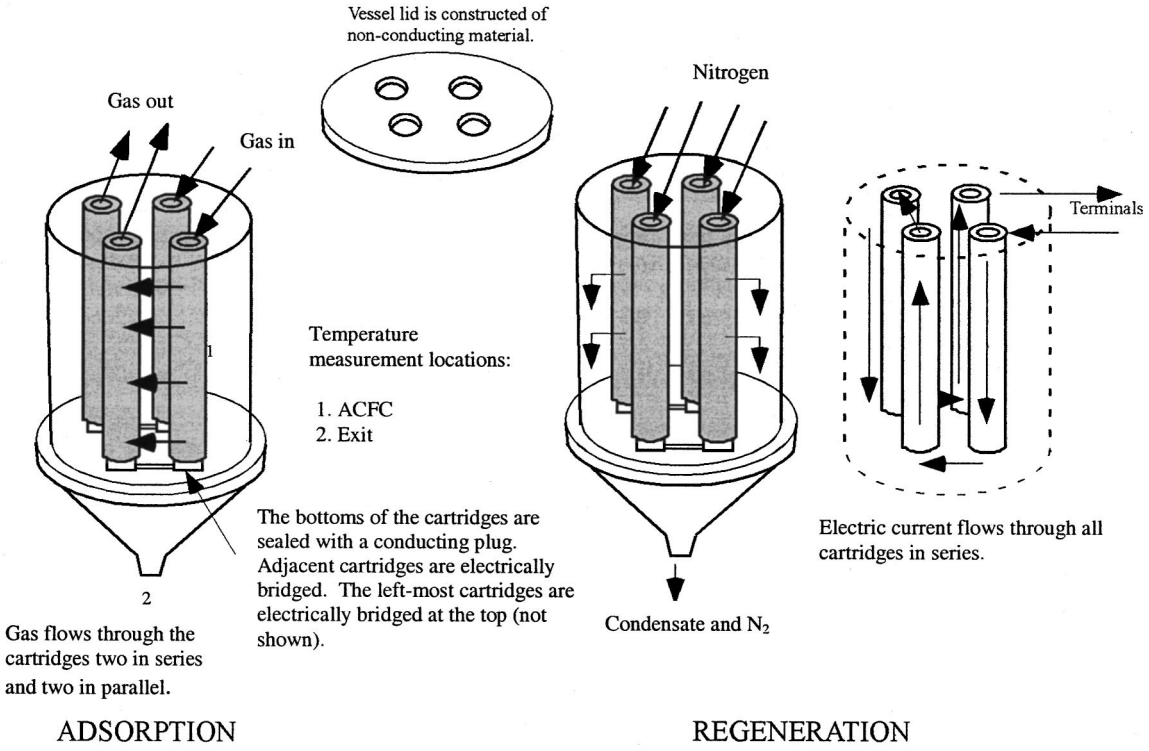

Fig. 1. Flow of gas and electrical current through adsorber

The adsorbate-laden air stream passed through a cylindrical adsorption vessel (15 cm long, 12.5 cm outside diameter, and 0.4 cm wall thickness) which contained 128.5 g of dried ACFC. The ACFC adsorbent used in this study was made from phenolic Novolac resin (ACC-5092-20, American Kynol, Inc.). The ACFC has a N_2 BET surface area of 1,970 m^2/g, with a micropore area of 1,890 m^2/g; thus, micropores comprise greater than 95% of the total surface area (Hsi et al. 2001). The areal density of the cloth is $128.7 \pm 21.8\ g/m^3$, and the electrical resistivity is $2.0 \times 10^{-3}\ \Omega \cdot m$ at ~22°C (Sullivan et al. 2001). A single sheet of ACFC was divided into four rolled cartridges of approximately equal mass. Each cartridge was 20.3 cm long, with 16 layers of cloth, and an outer cross-sectional area of 141 cm^2. The four cartridges were mounted vertically within the adsorption vessel such that gas flow passed through the walls of two cartridges in parallel, and then through another two cartridges in parallel (Fig. 1). The base of the adsorption vessel was constructed of aluminum and was conical to promote the flow of recovered liquid organic vapor through the exit of the vessel. Temperatures of the external surface of the ACFC cartridges and the N_2 purge stream as it exited the vessel were measured with thermocouples (Type J, Omega, Inc.).

N_2 gas (standard grade with 99.998% purity) at one actual L/min was used to purge the adsorption vessel of O_2 after the ACFC was saturated with organic vapor. Electrical power applied to the ACFC during electrothermal desorption was controlled with a silicon control rectifier (SCR, Robicon Series 440). The RMS current (I_{RMS}) was measured with an electric field donut (Fluke, Inc.), and the RMS voltage (V_{RMS}) was measured with a potentiometer (Fluke, Inc.).

Organic vapor formation during desorption was rapid, such that the vapor space in the vessel became saturated and liquid condensed on the vessel walls. This liquid flowed out the bottom of the vessel and was collected in an Erlenmeyer flask that was

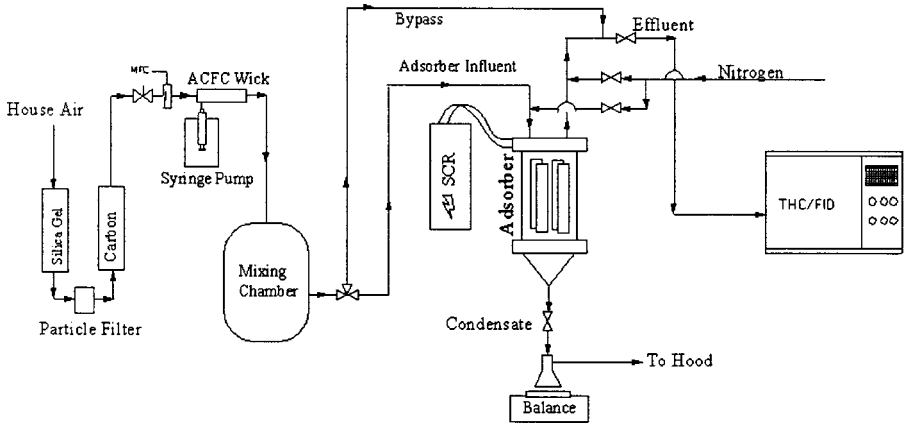

Fig. 2. System diagram for breakthrough curve tests

placed on a gravimetric balance (Acculab LT-3200) to measure the mass of liquid recovered. Desorption was performed without the aid of any ancillary cooling devices. Optimization of the amount of liquid recovered requires careful selection of material(s) for the vessel to allow for high heat transfer from the vessel to the ambient environment. However, in this study, the vessel walls were made of Pyrex to allow viewing of the desorption process, while the base was constructed of aluminum. Successful electrothermal-swing adsorption tests using a cylindrical vessel with an aluminum wall were completed by Sullivan et al. (2001).

Data acquisition and instrumentation control were carried out with a Keithley 500A Measurement and Control System with *ViewDac* software (version 2.10). A custom routine was programmed to monitor the concentration of organic vapor in the air stream exiting the adsorber and the temperature of the adsorber. This routine also controlled voltage application and valve switching.

Breakthrough curve tests were performed at ambient temperature (21 ± 2°C) and a total gas flow rate of 40.0 standard liter per minute (slpm) (standardized to 0°C, 101 kPa). A single-component organic-vapor-laden air stream of specified concentration passed through the ACFC adsorption vessel until the adsorption vessel was saturated with the adsorbate. The ACFC was then regenerated by purging the vessel with N_2 and applying electric power to the ACFC. Condensation of organic vapor on the vessel's internal walls was observed approximately one minute after power was applied to the ACFC, at which point the ACFC was approaching 50°C. Condensate then began to flow down the vessel walls, exiting the vessel to be collected in an Erlenmeyer flask. Electrical power was applied until the temperature of the ACFC cartridges reached 200°C, typically 210 s after the start of power application. Nitrogen continued to flow through the vessel for 2 min after the power application stopped, thereby purging the vapor space of N_2 that was saturated with organic vapor.

The ACFC's equilibrium adsorption capacity W is determined by Eq. (1) at saturation by integrating the area above the breakthrough curve

$$W=\frac{(\Sigma_{t=0}^{t_{\text{saturation}}}(C_0-C_t)Q\Delta t)}{m_{\text{ACFC}}} \tag{1}$$

where W = equilibrium adsorption capacity of ACFC; C_0 = inlet organic vapor concentration; C_t = concentration of organic vapor exiting the adsorber at time t; Q = inlet gas flow rate; m_{ACFC} = mass of ACFC in the vessel; and Δt = time interval in which C_t data were collected.

The *TPR* is calculated by Eq. (2) as the time required to achieve 5% breakthrough (t_5) divided by the time required to achieve 50% breakthrough (t_{50}) (LeVan et al. 1997)

$$TPR=t_5/t_{50} \tag{2}$$

Higher *TPR*s indicate a steeper breakthrough curve, where mass transfer limitations become less important. As the *TPR* approaches unity, the time needed to develop the mass transfer region becomes insignificant compared to the time needed to saturate the adsorber.

Adsorbers are typically taken off-line at or before 5% breakthrough. The *LUB*, as calculated in Eq. (3), is used to estimate the fractional length of bed that is not utilized at 5% breakthrough (McCabe et al. 1993)

$$LUB=1-M_{5\%}/M_{\text{adsorbed}}\approx 1-t_5/t_{\text{saturation}} \tag{3}$$

where $M_{5\%}$ = mass of organic vapor adsorbed at time t_5; and M_{adsorbed} = mass of organic vapor adsorbed at saturation, as calculated by Eq. (1) using mass adsorbed values. The smaller the *LUB*, the smaller the mass transfer zone and the smaller the mass transfer effects.

Liquid solvent recovery efficiency during electrothermal regeneration is quantified in Eq. (4) by computing the mass ratio of liquid organic vapor recovered from a single regeneration cycle (M_{liquid}) to the amount of organic vapor adsorbed during the preceding adsorption cycle

$$\text{Liquid solvent recovery efficiency}=M_{\text{liquid}}/M_{\text{adsorbed}} \tag{4}$$

Liquid solvent recovery efficiencies were less than unity because some organic vapor partitioned to the N_2 purge stream and was readsorbed to the ACFC at the end of the regeneration cycle. The amount of organic vapor in the purge stream (M_{N_2}) was determined by assuming that the purge gas was saturated with organic vapor at the average temperature of the exiting liquid, 29.5°C. The amount of organic vapor that remained adsorbed to the ACFC (M_{ACFC}) is quantified by the material balance in Eq. (5)

$$M_{\text{ACFC}}=M_{\text{adsorbed}}-M_{N_2}-M_{\text{liquid}} \tag{5}$$

As shown in Eq. (6), the total electrical energy E applied to the ACFC during desorption was calculated over time steps of 10 s.

$$E=\sum_n (I_{\text{RMS}})(V_{\text{RMS}})(\Delta t) \tag{6}$$

where Δt = time interval over which voltage was applied, 10 s; and n = number of 10 s intervals over which voltage was applied.

The total electrical energy applied during regeneration was divided by the total moles or mass of liquid collected to determine the *energy/liquid mole recovered* and *energy/liquid mass recovered*. Discounting vapor losses, energy consumed per unit mass of liquid recovered is reported to characterize the efficiency of electrothermal regeneration (without ancillary treatment) in recovering the organic vapor as a liquid for reuse. The *energy/mole adsorbed* was calculated by dividing the total amount of energy applied during regeneration by the moles of organic vapor gas that were adsorbed to the ACFC at equilibrium. The energy/mole adsorbed represents a minimum energy/mole for the system tested here if all of the adsorbate could be recovered as a liquid without consuming additional energy. The difference between the energy/mole recovered and energy/mole adsorbed quantifies the improvement that can be made by condensing all of the desorbed vapor during regeneration.

Results and Discussion

Evaluation of Activated Carbon Fiber Cloth Capture Efficiency

Equilibrium Adsorption Capacity

For all organic vapor adsorption tests, the initial outlet concentration from the adsorber was less than the detection limit of the FID, indicating greater than 99.9% removal of organic vapor by the ACFC. Equilibrium adsorption capacities were measured at concentrations ranging from 200 to 1,020 ppm_v, which translates to a relative pressure range of 1.5×10^{-3} to 2.2×10^{-2}. At the lower end of the relative pressure range tested (1.5×10^{-3} to 1.0×10^{-2}), the equilibrium adsorption capacities increased steeply with increasing relative pressure, consistent with a Type 1 isotherm (Fig. 3). As the relative pressure increased above 1.0×10^{-2}, there were smaller gains in the equilibrium adsorption capacity.

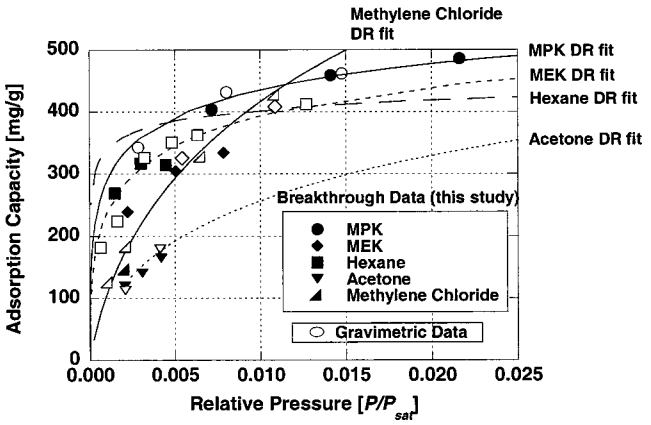

Fig. 3. Independently measured equilibrium adsorption capacities of organic vapors using breakthrough curves and Dubinin-Radushkevich fit predictions from gravimetric balance data

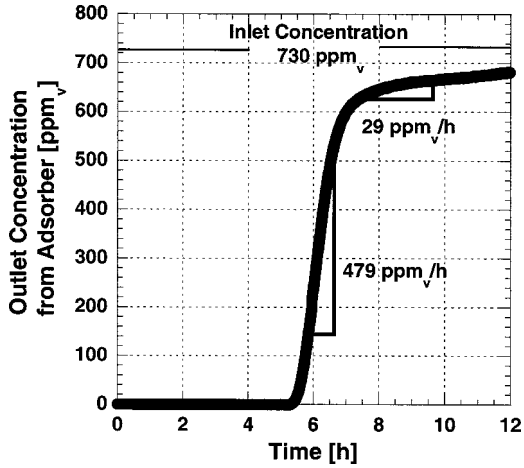

Fig. 4. This breakthrough curve, obtained for 730 ppm by volume methyl ethyl ketone in air, was typical of breakthrough curves obtained with the activated carbon fiber cloth adsorber

Of the compounds tested, MPK had the lowest saturation vapor pressure (3.47×10^3 Pa at 20°C) and the highest equilibrium adsorption capacity, ranging between 404 and 486 mg/g for concentrations between 253 and 765 ppm by volume. Hexane and MEK, with saturation vapor pressures of 9.33×10^3 and 1.60×10^4 Pa at 20°C, respectively, behaved similarly to each other, with equilibrium adsorption capacities ranging between 239 and 334 mg/g for concentrations between 206 and 732 ppm by volume. Acetone and methylene chloride had the highest saturation vapor pressures, 2.45×10^4 and 4.65×10^4 Pa at 20°C, respectively, and their equilibrium adsorption capacities were approximately one-third the capacity of MPK.

Two breakthrough tests were conducted for hexane at 475 ppm by volume. The calculated adsorption capacities were within 1% of each other. Two breakthrough tests were conducted for hexane at 710 ppm by volume. These results were within 4% of each other. The ACFC had undergone at least six adsorption/regeneration cycles between the original tests and the duplicate tests. The repeatability of these results indicates the ability of the ACFC to resist degradation.

The equilibrium adsorption capacity data determined in this study for MPK, MEK, hexane, acetone, and methylene chloride were compared with an independent gravimetric method (at 25°C) for the same lot of ACFC. This method is described here briefly for clarity, but is described in more detail (Ramirez et al. 2004). In the gravimetric method, a 3 g piece of ACFC was placed on a gravimetric balance (Cahn, Model C-2000) in a temperature-controlled vessel. As an adsorbate-laden N_2 stream passed through the vessel, the changing weight of the ACFC was monitored. When the ACFC reached a steady-state weight, the increase in weight was used to calculate the mass equilibrium adsorption capacity. The equilibrium adsorption capacities were used to determine the Dubinin-Radushkevich (DR) fitting parameters for each compound (Dubinin 1989). The DR equation describes physical adsorption in microporous activated carbon adsorbents based on a volume pore-filling model.

The adsorption capacities predicted by the DR fit were compared to the equilibrium adsorption capacities determined in this bench-scale adsorber study. Good agreement was seen for the MPK and acetone data, with discrepancies less than 8% between the DR predictions and the independent data obtained during this study (Fig. 3). For MEK, the DR overpredicted the capacity by 8% at the higher relative pressures tested, and by 17% at the lowest relative pressure tested. For hexane, there was good agreement between the gravimetric data and the breakthrough data; however, the DR fit (which was obtained for gravimetric data extending up to a relative pressure of 0.9) was not adequate for either set of data at low relative pressures. Differences between the breakthrough data and the DR predictions for hexane were as large as 30%. For methylene chloride, only one datum exists for comparison. The adsorption capacity for methylene chloride, as determined in this study, was 18% less than the DR-predicted adsorption capacity.

In all cases, the DR fit slightly overpredicted the adsorption capacity of the adsorber, perhaps indicating that full utilization of the ACFC was not achieved. The asymmetrical shape of the breakthrough curves obtained with the ACFC adsorber further indicates incomplete utilization of the ACFC. A typical curve, obtained for 730 ppm by volume MEK in air, is shown in Fig. 4. While the initial breakthrough has a very steep slope of 479 ppm by volume/h, the slope becomes shallow (29 ppm by volume/h) as the adsorber outlet concentration approaches the inlet concentration. It is speculated that the mounting brackets used to hold the ACFC in the adsorber vessel cause small sections of the cloth to be less accessible to the vapor-laden gas stream, thereby causing the asymmetry in the breakthrough curve.

Throughput Ratio

The arithmetic mean and standard deviation of the throughput ratio (*TPR*) for all of the tests performed was 0.91 ± 0.03 (Table 2). The arithmetic mean *TPR* is 9% less than the ideal value of unity, indicating that there were some mass transfer limitations in the system. The mean *TPR* is close to the experimentally determined maximum *TPR* of 0.95 that is practically achievable with this adsorption system (Sullivan et al. 2001).

The *TPR* data were located in two ranges (Table 2). Hexane, MPK, and MEK had an average *TPR* of 0.92 ± 0.01, while the compounds with higher saturation vapor pressures (acetone and methylene chloride) had a slightly lower mean *TPR* value of 0.87 ± 0.01. However, these results demonstrate that *TPR* changed by only 11% as the relative pressures of these compounds changed by 1,417%. The *TPR* was not sensitive to the wide range of relative pressures tested here. This result is encouraging for system applications that experience a wide range of relative pressures in their effluent gas streams.

Table 2. Summary of Experimental Results

Compound	Inlet gas phase concentration (ppm by volume)	Relative pressure (P/P_{sat})	Adsorption capacity (mg/g)	Throughput ratio (unitless)	Length of unused bed (unitless)	Energy/mole organic vapor recovered (kJ/mol)	Energy/mole organic vapor adsorbed (kJ/mol)	Isosteric heat of adsorption[a] and (*heat of vaporization at boiling point*)[b] (kJ/mol)
MPK	253	7.4×10^{-3}	404	0.91	0.10	375	303	
	499	1.5×10^{-2}	459	0.93	0.09	332	271	(*33.4*)
	765	2.2×10^{-2}	486	0.93	0.12	327	262	
MEK	206	2.2×10^{-3}	239	0.91	0.10	544	379	49.9
	471	5.1×10^{-3}	305	0.92	0.13	423	317	(*31.3*)
	732	7.9×10^{-3}	334	0.92	0.11	419	233	
Hexane	233	1.5×10^{-3}	269	0.92	0.16	629	396	
	475	3.0×10^{-3}	317	0.94	0.09	584	330	(*28.9*)
	710	4.5×10^{-3}	308	0.92	0.11	546	324	
Acetone	503	2.1×10^{-3}	120	0.88	0.19	1,367	516	47.2
	752	3.1×10^{-3}	141	0.88	0.17	1,009	462	(*29.1*)
	1,020	4.2×10^{-3}	165	0.87	0.18	924	487	
Methylene chloride	960	2.1×10^{-3}	147	0.85	0.22	4,698	498	(*28.1*)

Note: MPK=methyl propyl ketone; MEK=methyl ethyl ketone.

[a]Ramirez et al. (2004).

[b]Weast (2000).

Length of Unused Bed

Fractional length of unused beds (*LUB*s) ranged from 0.09 to 0.22 (Table 2). As with *TPR* values, there are two distinct regions observed for *LUB* values. For MPK, MEK, and hexane the arithmetic mean and standard deviation of the *LUB* were 0.11 ± 0.02. For acetone and methylene chloride the *LUB* was 0.19 ± 0.02, so that the fractional *LUB* was almost twice as long, indicating greater mass transfer effects. However, the *LUB* was still limited to less than 0.22 for the range of relative pressures. The *TPR* and *LUB* results indicate that the mass transfer zone within the ACFC is only slightly dependent on the relative pressure of the organic vapors tested here.

Evaluation of Activated Carbon Fiber Cloth Regeneration Efficiency

Liquid Solvent Recovery Efficiency

Overall, the liquid solvent recovery efficiency (Fig. 5) followed the same trend as the equilibrium ACFC adsorption capacity (Fig. 3). The liquid recovery fraction increased with increasing relative pressure of the inlet organic vapor stream, with the recovery fraction asymptotically approaching a maximum value of ~0.80, based on two data points for MPK at relative pressures larger than 0.010.

Partitioning of the organic vapor between M_{adsorbed}, M_{N_2}, and M_{liquid} during regeneration demonstrates that the mass fraction of organic vapor remaining in the adsorption vessel was fairly constant for all of the tests (Fig. 6). However, as the saturation vapor pressure of the organic vapor increased, there was a concomitant loss of organic vapor to the N_2 purge gas stream, causing smaller liquid recovery efficiencies. Methylene chloride had the lowest overall solvent recovery fraction of 0.11, due to the preferential partitioning of the compound into the gas phase.

In a dual-adsorber system, the N_2 purge stream would be recycled to the on-line adsorber. Increasing concentrations of organic vapor in the N_2 purge stream would decrease the breakthrough time for the online adsorber. A similar automated adsorption system with two ACFC cartridges per vessel was operated with an MEK/air stream to evaluate the reduction in breakthrough time (t_5) caused by the retention of adsorbate in the vessel after electrothermal regeneration and the recirculation of organic vapor in the recycle stream (Sullivan et al. 2004). There was a 22% reduction in t_5 for the second adsorption cycle compared to the first adsorption cycle that initially contained no organic vapor in the ACFC. For organic vapors with high saturation vapor pressures (e.g., acetone and methylene chloride), the breakthrough time may become smaller than the time needed for desorption and cooling. In such cases, continuous operation of a dual-adsorber system would not be possible without using more adsorbent in each vessel or treating the exit stream (e.g., chilling).

Energy/Mole Adsorbed versus Energy/Liquid Mole Recovered

The total electrical energy supplied for desorption of the ACFC ranged from 1.1×10^2 to 1.9×10^2 kJ for the system and com-

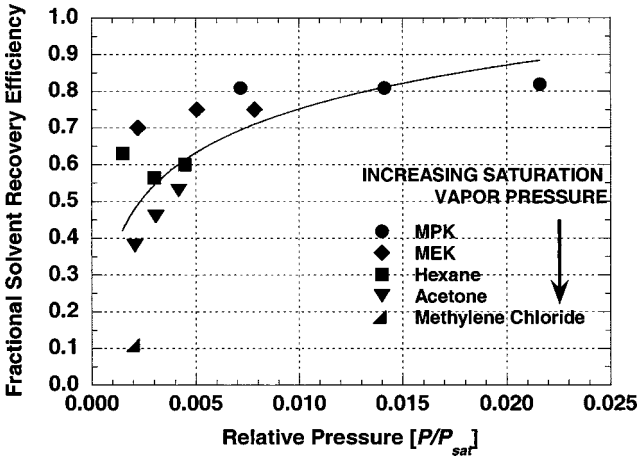

Fig. 5. Dependence of liquid solvent recovery efficiency during electrothermal regeneration on relative pressure of organic vapor in inlet gas stream

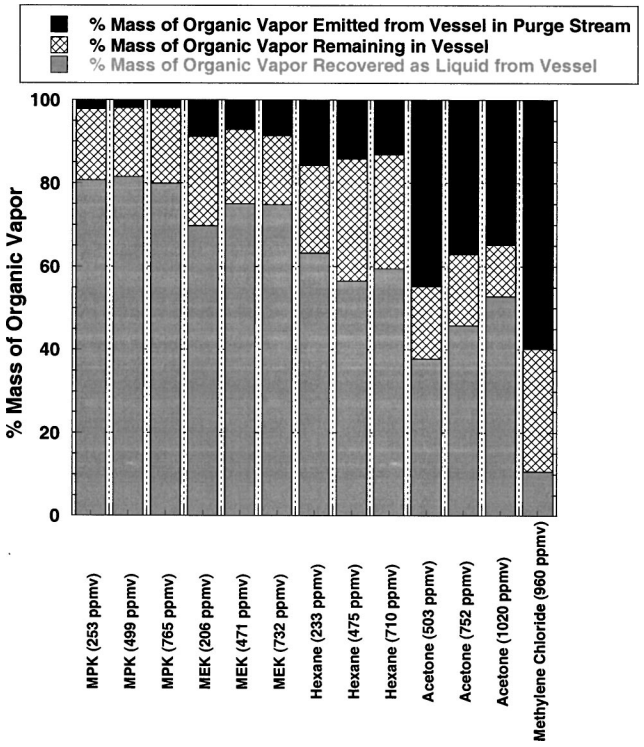

Fig. 6. Partitioning of organic vapor during electrothermal regeneration between the N_2 purge stream, the activated carbon fiber cloth (ACFC), and the recovered liquid. The horizontal axis categories refer to the conditions at which the ACFC adsorption vessel was saturated prior to regeneration.

pounds evaluated here. Total electrical energy per liquid mole of organic vapor recovered increased exponentially from 327 to 4,698 kJ/mol with decreasing relative pressure of the inlet gas stream (Table 2 and Fig. 7). The energy/liquid mole recovered for methylene chloride was three times larger than described by the curve fit because of the small liquid recovery achieved from desorption.

For methylene chloride, which has a higher saturation vapor pressure and lower equilibrium adsorption capacity, the calculated amount of vapor in the N_2 stream has an even greater dependency on the temperature compared to the other vapors tested here. Furthermore, it is unclear whether equilibrium was established at the gas/adsorber wall interface for the methylene chloride. During desorption, the methylene chloride formed a visible fog that occupied the annular space between the ACFC and the vessel walls. The other compounds did not have a visible fog, except on the vessel walls. Film versus dropwise condensation mechanisms may have played a role in the degree of condensation achieved for methylene chloride (Incopera and Dewitt 1981).

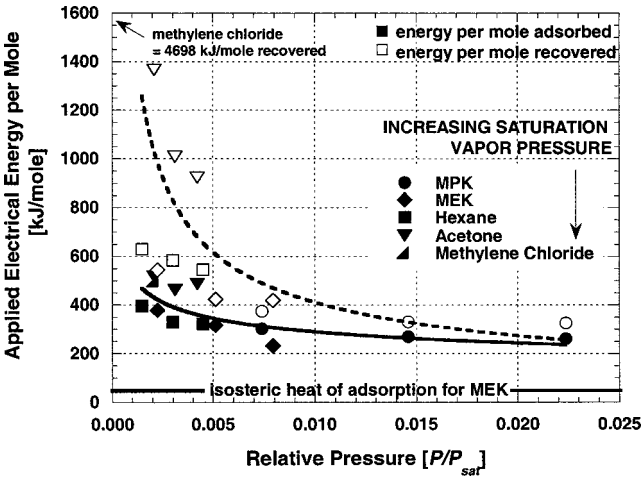

Fig. 7. Energy/mole adsorbed and energy/mole recovered as a function of relative pressure of the inlet gas stream

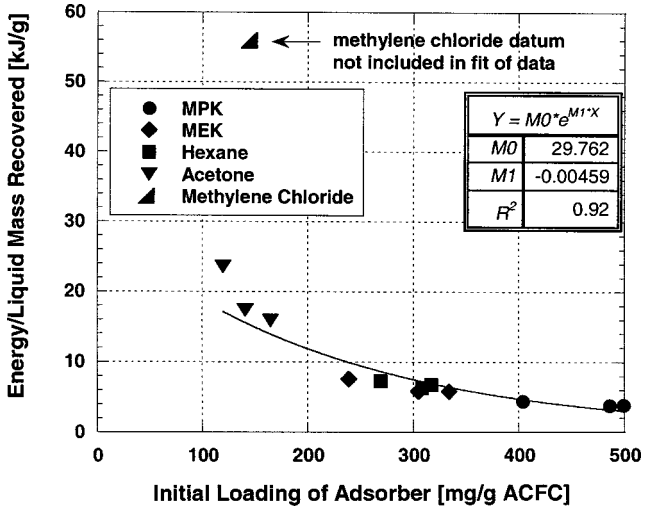

Fig. 8. Energy/liquid mass recovered for five organic vapors as a function of initial organic vapor loading of adsorber

The total energy/mole adsorbed for each of the experiments ranged from 233 to 516 kJ/mol. For the experimental conditions tested, the total energy/mole adsorbed represents the minimum amount of energy/mole needed to recover all of the organic compound. The values for energy/mole recovered were greater than the values for energy/mole adsorbed because 100% liquid recovery was not achieved. As the relative pressures of the compounds decreased and fractional liquid recovery efficiency decreased, the disparity between the energy/mole adsorbed and energy/mole recovered increased (Fig. 7).

The energy/liquid mass recovered increased exponentially with decreasing initial adsorber loading (Fig. 8). For example, MPK had a higher initial adsorber loading than MEK, so more total energy was needed to desorb MPK. However, the energy/liquid mass recovered was smaller for MPK because it had a higher fractional recovery of liquid.

Comparison of Energy/Mole Recovered to Isosteric Heat of Adsorption

Assuming a completely reversible process, the isosteric heat of adsorption represents the ideal minimum energy needed to desorb an adsorbate. The isosteric heat of adsorption for MEK is 49.9 kJ/mol (Ramirez et al. 2004). The energy/mole of MEK adsorbed depended on the inlet gas concentration, but on average it was about six times higher than the isosteric heat of adsorption (Table 2). For acetone, the isosteric heat of adsorption is 47.2 kJ/mol (Ramirez et al. 2004), and the energy/mole of acetone adsorbed was on average about ten times higher than the isosteric heat of adsorption. This comparison shows that, as the saturation vapor pressure of the compound increases, there is an increasing disparity between the energy used to electrothermally desorb organic vapor from the ACFC and the theoretical minimum energy.

Summary and Conclusions

The equilibrium adsorption capacity increased as the relative pressure increased for the activated carbon fiber cloth adsorbent and organic vapors tested here. The organic vapors having lower saturation vapor pressures (MPK, MEK, and hexane) had an average throughput ratio (*TPR*) of 0.92 ± 0.01, while the higher saturation vapor pressure organic vapors (acetone and methylene chloride) had an average *TPR* of 0.87 ± 0.01. The length of unused bed (*LUB*) gave the same trends as the *TPR*. These results indicate that the current configuration of the adsorber is effective for these compounds; however, as the saturation vapor pressure increases, there are incentives to modify the adsorber by increasing the activated carbon content within the adsorber.

After the ACFC was saturated with organic vapor, it was electrothermally regenerated to determine the fractional recovery efficiency of liquid organic vapor and the energy used to regenerate the ACFC. In general, the fractional recovery of liquid increased as the organic vapor relative pressure in the feed stream increased. Partitioning of organic vapor to the N_2 purge stream became significant for the higher-saturation-vapor-pressure compounds acetone and methylene chloride. Breakthrough times for these compounds may become shorter than the time needed for regeneration in a dual-vessel system because the N_2 purge stream would be recycled to the vessel that is adsorbing organic vapor from the incoming air. In such a case, chilling of the low-flow-rate N_2 purge stream would be beneficial.

The energy/liquid mass recovered increased exponentially as the initial mass loading of the adsorbent decreased. Comparison of the energy/mole adsorbed to the isosteric heat of adsorption indicates that, as the saturation vapor pressure of the compound increased, there was an increase in the disparity between these two parameters. This result suggests the need for additional work to produce a convergence of these two parameters.

Despite differences in results for the relative pressures of organic vapors tested here, the ACFC had significant adsorption capacities for all five compounds studied. However, the combined effect of low liquid recovery and high energy usage may facilitate retrofits to the existing ACFC system for its application with compounds at lower relative pressures. Possible retrofits include increasing the mass content of ACFC per unit volume of the vessel and chilling the recycle of the low-flow-rate N_2 purge gas. For lower-saturation-vapor pressure compounds, the ACFC electrothermal-swing adsorption system is a very promising candidate for capturing dilute organic vapors from air streams and producing liquid organic vapor for reuse in the process that produced the vapor.

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